



Catalytic hydrodechlorination of 1,2,4-trichlorobenzene over Pd/Mg(Al)O catalysts

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ABSTRACT

Catalytic hydrodechlorination (HDC) is an efficient way to remove chloride species from chlorinated hydrocarbons. Hydrodechlorination reaction of 1,2,4-trichlorobenzene was studied over a series of palladium (1 wt.%) catalysts supported on calcined Mg/Al hydrotalcite-like materials (HT) prepared with different Mg/Al ratios. The fresh catalysts were characterized using ICP-OES, XRD, N₂-physisorption, H₂-chemisorption, TPR, and TEM. It has been observed that the activity, stability and selectivity of the catalysts in the hydrodechlorination reaction of 1,2,4-trichlorobenzene were strongly dependent on the Mg/Al molar ratio in the Mg(Al)O support. The sample with Mg/Al ratio of 4 exhibited the highest activity and selectivity towards total hydrodechlorination reaction giving benzene. Rehydration of the calcined hydrotalcite catalyst resulted in an enhancement of the hydrodechlorination performance. The spent samples were characterized by TPO/MS, TGA and ESEM-EDS techniques. Based on our results it was revealed that catalyst deactivation was mainly due to coke formation. The amount of coke decreased with the base character of the support. The amount of coke formed during the reaction can be eliminated by combustion recovering the initial activity.

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1. Introduction

Organohalogenated compounds are hazardous pollutants contained in various waste oils and organic liquids. They have been used widely in the manufacture of refrigerants, herbicides, dyes, wood protectors, plant growth regulators, dye carriers, pesticide intermediate, heat-transfer medium and dielectric fluid in transformers. The options of their disposal include incineration, pyrolysis, catalytic steam reforming, biological treatment and catalytic oxidation. However all these processes are associated with drawbacks like high toxic emissions for instance formation of dioxins [1], low conversion and high energy expense. Catalytic hydrodechlorination (HDC) is then becoming an attractive method for the treatment of chlorinated organic wastes [2–4]. HDC operates at low temperature and pressure, forms no harmful side-products and could eventually be selective towards chloride removal [5]. This process is efficiently catalyzed by noble metal catalysts on various supports under mild conditions. The best catalytic systems contain palladium [4]. A characteristic of HDC is the occurrence of fast deactivation, observed with most substrates.

Catalytic decay in gas-phase hydrodechlorination has been linked to different phenomena such as poisoning of the active phase by the HCl formed in the reaction [6–9], particle sintering [10], and coke deposition [11,12].

Particle sintering and coke formation are expected to be affected by the choice of the support. The common supports employed for HDC are activated carbon, MgO, SiO₂, and Al₂O₃. The acid-base character of the support has an influence on the catalytic properties of the metal for the conversion of chlorobenzene to cyclohexane: Hashimoto et al. reported a higher selectivity towards cyclohexane for Pd supported on chlorinated aluminas [13], and on silica-alumina [13]. The effects of the modification of Pd/C by basic additives have been linked to chloroarene dissociation and surface charge effects [14]. A different charge at the Pd surface has been evidenced by the shift of the infrared band of CO in the case of Pd and Pt supported on hydrotalcites [15–17]. Indeed a clear effect of basic supports has been reported on the catalytic properties for reactions involving arylchlorides, such as Heck reactions, in which the reactivity increases when hydrotalcites [18] or MgLa mixed oxides [19] are used as supports. An effect on deactivation is also expected to change: an increase of the electron density at the surface induced by the support should decrease the adsorption of Cl which is an electro-donor. Moreover coke formation catalyzed by acid-base mechanisms should also be

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affected. Surprisingly basic supports have scarcely been used for dechlorination, probably because they were expected to be neutralized by the HCl produced by the reaction. We report here the hydrodechlorination reaction of 1,2,4-trichlorobenzene over hydrotalcite-like supported Pd. The activity of palladium supported on calcined Mg/Al hydrotalcites with different basic character was studied. The effect of rehydration–reconstruction of the supports together with Pd catalyst was investigated on the catalytic activity and stability. Finally the source and nature of deactivation on spent catalysts were studied. The activity and stability of the catalyst was also assessed with the meixnerite-like phase obtained by rehydration of calcined hydrotalcite.

2. Experimental

2.1. Preparation of the support

The hydrotalcite-like (HT) compound was prepared by coprecipitation of suitable amounts of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ (Mg/Al molar ratio of 2, 3 and 4) with solutions of NaOH (2.0 M) as stated elsewhere [20]. HT was prepared with constant stirring maintaining the pH 10. The addition of the alkaline solution and pH were controlled by pH-STAT Titrino (Metrohm). The suspension was stirred overnight at room temperature. The resulting gel was centrifuged and washed several times thoroughly with distilled water ($Na < 100$ ppm) until the pH of the centrifuged material is neutral and also to remove any free sodium ions. The sample was dried in an oven overnight at 393 K and then heat-activated in air flow at 723 K for 6 h (heating rate: 1 K min^{-1}) to yield the $Mg(Al)O$ mixed oxide. Calcined hydrotalcites with different Mg/Al molar ratios of 2, 3 and 4 prepared were labeled as HT-21, HT-31 and HT-41, respectively. The chemical compositions of the samples were determined by ICP-OES in a PerkinElmer Plasma 400.

2.2. Catalyst preparation

The palladium $Mg(Al)O$ catalysts were prepared by two procedures. Pd (II) acetylacetone ($Pd(C_5H_7O_2)_2$) was used as Pd precursor. In the first one, the calcined solid was introduced in a toluene solution of palladium (II) acetylacetone for 12 h, dried at 398 K under vacuum, and calcined in air flow at 673 K for 2 h. The calcined material was reduced at 623 K under hydrogen flow for 2 h before reaction. The palladium catalysts were denoted as Pd-HT-41, Pd-HT-31 and Pd-HT-21. In the second procedure 250 mg of calcined Pd-HT-41 catalyst was first reduced at 623 K under hydrogen flow ($60\text{ cm}^3\text{ min}^{-1}$) and then rehydrated in gas-phase at 373 K using argon (flow 40 ml min^{-1}) saturated with deionized water for 18 h in situ. This catalyst hereafter was named as Pd-HTR-41.

2.3. Catalyst characterization

2.3.1. ICP-OES

The chemical composition of the samples was determined by ICP-OES with a PerkinElmer Plasma 400 instrument.

2.3.2. Powder X-ray diffraction patterns

The XRD analysis of the materials were recorded using Siemens D5000 diffractometer (Bragg–Bentano parafocusing geometry and vertical θ – θ goniometer) fitted with a grazing incident ($\omega = 0.52^\circ$) attachment for thin film analysis and scintillation counter as a detector. The samples were dispersed on Si (5 1 0) sample holder. The angular 2θ diffraction range was between 5° and 90° . The data were collected with an angular step of 0.03° at 12 s per step and sample rotation. Cu K α radiation ($\lambda = 1.54056\text{ \AA}$) was obtained

from a copper X-ray tube operated at 40 kV and 30 mA. The crystalline phases were identified using the JCPDS files.

2.3.3. N_2 -physisorption adsorption–desorption isotherms at 77 K

It was measured using Micromeritics ASAP 2000 surface analyzer and BET surface areas were calculated. Before analysis, all the samples were degassed in vacuum at 393 K for 6 h.

2.3.4. Hydrogen-chemisorption

The analysis was performed under static volumetric conditions with a Micromeritics ASAP 2010 apparatus. Prior to the measurement, the sample was evacuated at 373 K for 1 h, treated in flow pure hydrogen ($30\text{ cm}^3\text{ min}^{-1}$) at 623 K for 3 h, evacuated at 623 K for 1 h, cooled down to 373 K and evacuated for 30 min. Finally the chemisorption analysis was performed at 373 K. The double isotherm method was used to determine the amount of irreversible adsorbed hydrogen which allows calculating the apparent metallic dispersion (H/Pd) assuming an adsorption stoichiometry of H:Pd = 1:1. From the first isotherm the total volume of hydrogen adsorbed was obtained. The sample was evacuated (about 10^{-6} Torr) again at the chemisorption analysis temperature for 10 min for back sorption measurements in order to obtain the volume of hydrogen reversibly adsorbed. The linear zone of each isotherm was extrapolated to zero pressure in order to estimate the volume of the strong hydrogen adsorbed.

2.3.5. Transmission electron microscopies (TEM)

TEM operated at 80 kV (JEOL JEM-2000EX II) was taken to analyze the morphology and dispersion of our catalysts. Samples were dispersed in alcohol in an ultrasonic bath and a drop of supernatant suspension was poured onto a holey carbon-coated grid and dried completely before the measurements were taken.

2.3.6. H_2 -temperature-programmed reduction (TPR)

TPR studies were performed in a ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector (TCD). The catalysts were treated in O_2 for 1 h at 573 K before TPR analysis. The samples were then purged with argon flow before the TPR analysis. The analysis was carried out using a 3% H_2/Ar gas flowing at 20 ml min^{-1} by heating from room temperature to 823 K with a ramp of 10 K min^{-1} . Water produced during TPR was trapped in $CaO + Na_2O$ (Soda lime) before reaching the TCD.

2.3.7. CO_2 -TPD

The basic properties of the materials were also determined by TPD of CO_2 using a TPDRO 1100 (Thermo Finnigan), equipped with a programmable temperature furnace and a TCD detector. The catalysts were first purged using He 373 K for 45 min. The CO_2/He (3%) adsorption was carried out by heating the sample from 303 to 373 K flowing at 20 ml/min. Finally the weakly adsorbed CO_2 were purged using He flowing at 100°C for 45 min. Typically, ca. 150 mg of sample were placed between plugs of quartz wool in a quartz reactor, and the desorption of CO_2 was measured by heating the sample from room temperature to 1123 K at 10 K min^{-1} under a He gas flow ($20\text{ cm}^3\text{ STP min}^{-1}$).

2.3.8. Temperature-programmed desorption and oxidation (TPDO/MS)

It was carried out for spent catalysts (washed with ethanol) in ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector. Previously we have seen that no effect in reactivation of the spent catalyst by washing with ethanol. Before analysis the catalysts were pretreated using He-TPD/MS heating from room temperature to 623 K at 20 K min^{-1} and maintained for 30 min at this temperature to remove ethanol and other species.

Then the sample was cooled to room temperature and TPO/MS analysis was carried out.

2.3.9. Thermogravimetric analysis (TGA)

It was performed in order to quantify the amount of carbonaceous deposits for the spent catalysts after hydrodechlorination reaction at 473 K. Thermogravimetric analyses was carried out on a PerkinElmer TGA 7 microbalance with an accuracy of $\pm 1 \mu\text{g}$ which was equipped an automatically programmed temperature controller. Prior to analysis the spent catalysts were treated with Argon (20 ml min^{-1}) heating at 5 K min^{-1} from room temperature to 1173 K and then cooled down again to room temperature. This step was adopted to eliminate all inorganic carbon species. In the sequence the sample was heated up to 1173 K in oxygen flow (5 K min^{-1} , 20 ml min^{-1}) and the weight loss was recorded. The TGA studies of the spent catalysts were performed after 20 h on stream for Pd-HT-21 and Pd-HT-31, whereas for Pd-HT-41 and Pd-HTR-41 it was of 60 h of time on stream in order to detect the amount of carbonaceous deposits.

2.3.10. Environmental scanning electron microscopy analysis (ESEM) combined with energy-dispersive spectroscopy (EDS)

Analysis of the spent catalysts was carried out in a FEI QUANTA 6000 scanning microscope operating at an accelerating voltage of 20 kV with 10 mm of working distance (WD) sample.

2.3.11. Catalytic activity

The hydrodechlorination of 1,2,4-trichlorobenzene was studied in a fixed-bed flow tubular reactor (10 mm i.d., 200 mm long) using 0.25 g of catalyst at atmospheric pressure and at different temperatures ranging from 323 to 523 K. The catalyst sample was packed at the center of the reactor between to plugs of wool. Prior to reaction the catalyst was reduced in situ by hydrogen flow at 632 K for 2 h. 1,2,4-Trichlorobenzene was injected continuously with help of a pump and H_2 ($>99.9\%$ pure) and the molar ratio of $\text{H}_2/1,2,4$ -trichlorobenzene was maintained 180 to favour 1,2,4-trichlorobenzene transport at room temperature [21]. The stabilities of the catalysts were studied over a period of 72 h of reaction at 473 K. Two space velocities were used to compare their stability. $15.6 \text{ mg min mmol}^{-1}$ was used for comparing the catalytic activities of Pd-HT-21, Pd-HT-31 and Pd-HT-41 and $61.6 \text{ mg min mmol}^{-1}$ for comparing the catalytic activities of Pd-HT-41 and Pd-HTR-41. The product mixture was collected in an ice-cold trap and analyzed by gas-chromatograph (CG-17A, MS Shimadzu instruments) equipped with flame ionization detector (FID) and capillary column. Before characterization, the spent catalysts were washed with ethanol to remove the solvent hexadecane and dried at 323 K for 48 h.

3. Results

3.1. Catalyst characterization

Table 1 shows the magnesium and aluminum loading in the samples as determined by ICP-OES. The nominal Mg and Al species contents analyzed in the solids were very similar indicating the efficiency of the preparation. Hereafter we have referred to nominal Mg/Al molar ratio to describe the experimental results and the discussion along the manuscript. Specific surface areas of the supported palladium catalysts (Pd-HT) are given in Table 1. All samples are mesoporous. Calcined hydrotalcite supports have surface areas in the range of 169 and $196 \text{ m}^2 \text{ g}^{-1}$. A slight decrease in surface area of the catalysts was observed when the Mg/Al ratio increases. Similar trend was observed for Pd-HT catalysts with surface area range of $165\text{--}185 \text{ m}^2 \text{ g}^{-1}$. When the corresponding

Table 1
Some characteristics of the catalysts

Sample	Mg/Al ^a	S_{BET} (m^2/g) ^b	H/Pd ^c	Pd particle size (nm) ^d
HT-21	1.9	196	–	–
HT-31	2.8	187	–	–
HT-41	3.7	169	–	–
Pd-HT-21	1.9	185	0.19	4.75
Pd-HT-31	2.8	179	0.06	3.82
Pd-HT-41	3.7	165	0.04	3.62
Pd-HTR-41	3.7	104	–	–

^a ICP-OES.

^b Specific surface area.

^c Pd exposed at the surface obtained by hydrogen chemisorption.

^d From TEM.

Pd-HT-41 was rehydrated in a flow of argon saturated with water the BET surface area dropped, as expected, from 169 to $100 \text{ m}^2 \text{ g}^{-1}$.

X-ray diffraction patterns of the different calcined hydrotalcite supports, and fresh palladium catalysts (Pd-HT) are shown in Fig. 1. The XRD profiles of the support materials calcined at 723 K are shown in Fig. 1a. In general the XRD patterns of the calcined materials are characteristic of well-defined crystallized mixed oxide with periclase (MgAlO_x) structure shown at (1, 1, 1), (2, 0, 0)

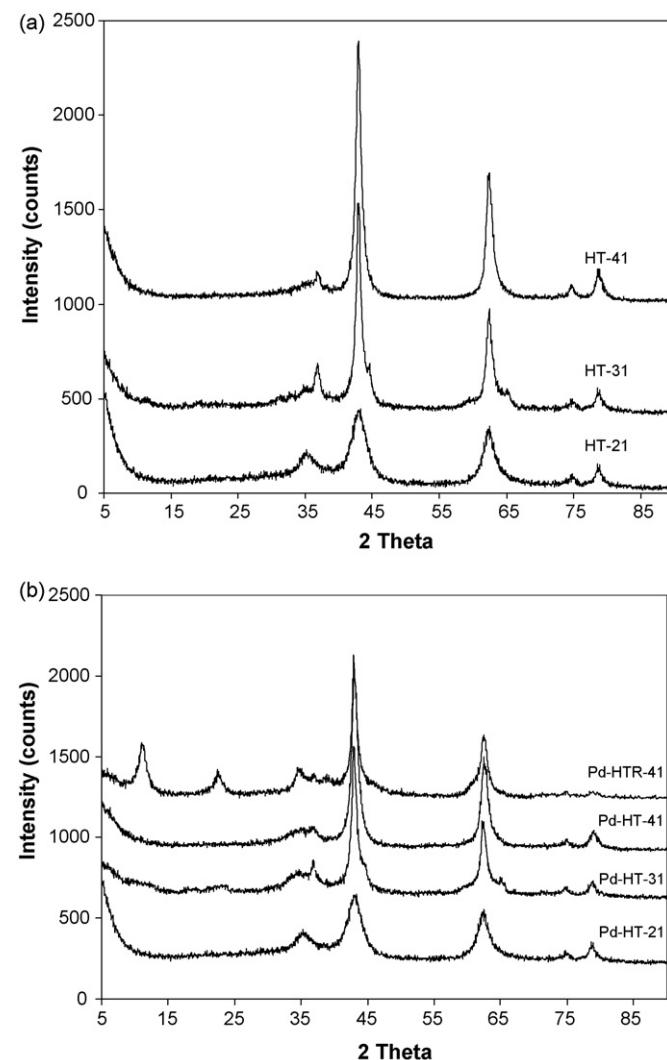


Fig. 1. X-ray diffraction of the calcined hydrotalcite materials. (a) Different supports, and (b) palladium catalysts (Pd-HT).

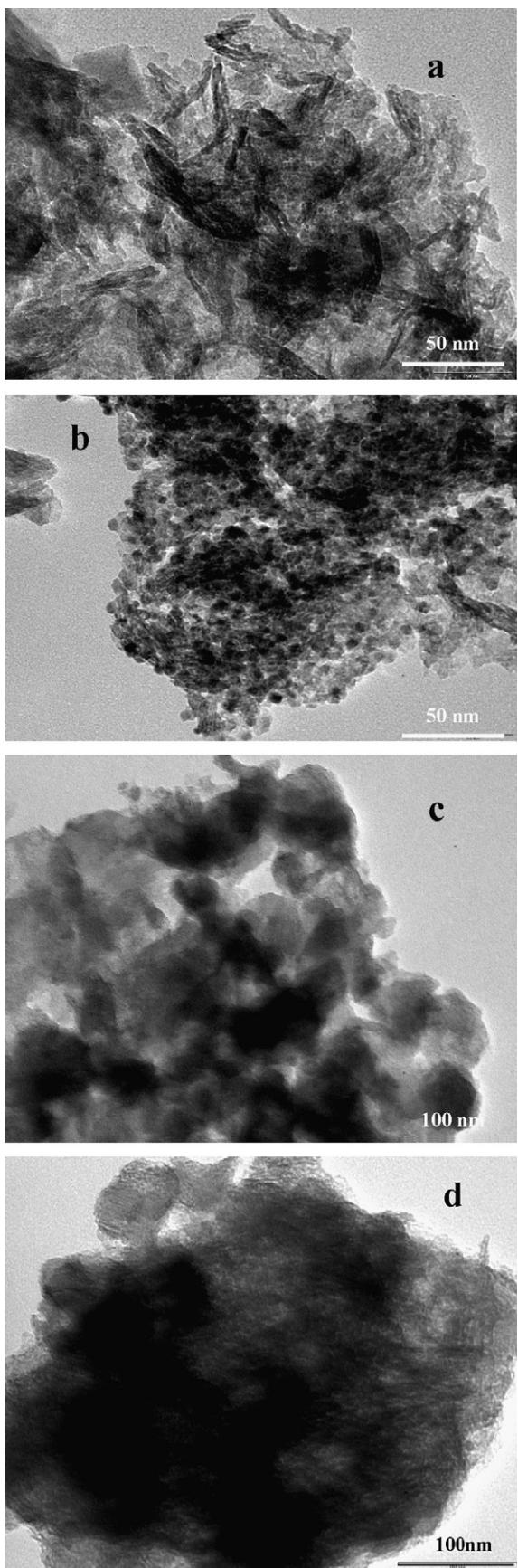


Fig. 2. TEM image of a representative sample: (a) support material (HT-21), (b) Pd-HT-21 sample and (c, d) spent Pd-HT-21 catalyst.

and (2, 2, 0), (3, 1, 1) and (2, 2, 2) (JCPDS file: 87-0653). Diffraction patterns of calcined HT samples showed no residual hydrotalcite or hydroxide phase, confirming that heating at 723 K leads to complete decomposition of hydrotalcite samples. The XRD profile for the Pd-HT (Fig. 1b) samples did not reveal distinct peaks corresponding to palladium species. As the Pd loading was rather low, the absence of diffraction line of Pd species may be due to the fact that the corresponding Pd particles are too small to be detected by the XRD instrument. It is worth noting that the impregnation of palladium species on the support material did not change the periclase phase.

The TEM technique was subsequently used to evaluate the size of the reduced palladium particles. The TEM images for HT-21, Pd-HT-21 and spent Pd-HT-21 catalysts are shown in Fig. 2a–c respectively. Fig. 2a shows the TEM image for the support material with a platelet morphology characteristic of derived hydrotalcite materials. Fig. 2b shows the typical morphology of a Pd crystallite. Palladium particles are clearly visible as dark dots uniformly dispersed on the surface of support. TEM was used to determine the crystal size of palladium particles. The diameter of a crystallite was taken as an average of the longest and shortest diameter, and over 200 individual crystallites were measured. The mean diameter values of the Pd particles in the catalysts are reported in Table 1.

The TEM micrographs of the Pd-HT-21 catalysts revealed the appearance of relatively narrow size distribution (Fig. 2b) showing Pd crystallites with mean diameter of 4.7 nm and only few particles over this size were observed. For Pd-HT-41, the size distribution was also narrow and the overall crystallite dimensions were similar. It follows that the Pd particles may be considered as fairly monodispersed for all samples supporting the fact that no Pd crystalline phase was detected in the XRD analysis. The TEM images obtained for the spent Pd-HT-21 catalyst is shown in the Fig. 2c. This material seems to be covered by some fouling species. By energy-dispersive spectroscopy analysis carbon was detected on the surface of the spent catalyst, but not on the fresh one, as observed in Fig. 3. The presence of carbonaceous species in the spent samples may suggest that the deactivation originated from coking during hydrodechlorination.

The ability of a catalyst to dissociate molecular hydrogen into its hydrogen atoms so that it can easily attack C–Cl bond is an important property for the reaction of hydrodechlorination. As a result hydrogen chemisorption was measured for the three catalysts Pd-HT-41, Pd-HT-31, and Pd-HT-21. The H₂-chemisorption results are shown in Table 1 in terms of the percentage of Pd exposed at the surface. Based on these results, it appears that as the amount of magnesium species in the support increases, the uptake of hydrogen decreases.

TPR profiles of palladium catalysts Pd-HT-41, Pd-HT-31 and Pd-HT-21 are shown Fig. 4. They show a major reduction peak at temperature around 600 K. The reduction temperature depends on the degree of interaction between the active species and the support. The small peaks at 300–420 K can be assigned to reduction of PdO crystallites to Pd⁰ metal [22]. The second peak between 593 and 603 K indicated further consumption of hydrogen on all the catalysts, and corresponds to palladium strongly interacting with the support, for instance as cations. A peculiar behavior of Pd concerns its ability to form a Pd hydride species (β -H_xPd) at ambient temperature. No peak corresponding to β -H_xPd hydride decomposition was observed in the samples. This can be ascribed to the rather small size of palladium particles, since Boudart and Hwang [23] reported that the solubility of hydrogen decreased with Pd particle size.

TPD-TPO/MS analysis for the spent catalysts after 10 h on stream for Pd-HT-21 and Pd-HT-31 and after 60 h on stream for Pd-

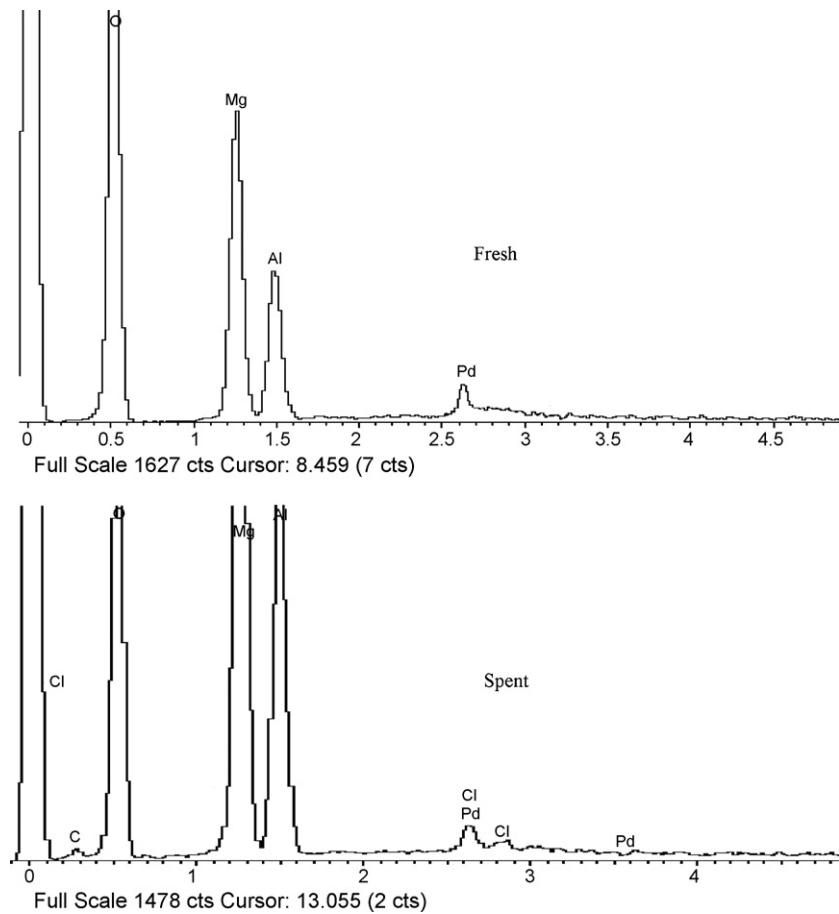


Fig. 3. Energy-dispersive spectroscopy (EDS) analysis on the surface of the fresh and spent Pd-HT-21 catalyst.

HT-41 and Pd-HTR-4 catalysts, are reported on Fig. 5. The spent catalysts were analyzed first using the He-HTPD/MS, followed by TPO/MS in order to investigate the nature of the species retained at the surface. The MS profiles of He-TPD for all the spent catalysts showed no signal in the mass spectroscopy (MS) presenting no evolution of deposited species on the used catalysts as depicted in Fig. 5. It can be pointed out that no Cl evolution was observed. By contrast, TPO/MS profiles show the presence of

signals corresponding to CO_2 , CO , and C , with consumption of oxygen. This is a clear evidence of the formation of “coke” at the surface.

The TPO profiles of these used catalysts are depicted in Fig. 6. The profile for Pd-HT-21 catalyst exhibits two peaks at 629 and 729 K suggesting two different sites for deactivation. The TPO profiles for the other catalysts are characterized by a single peak. These results suggest that the species deposited on the spent catalysts is coke.

The results of TGA measurements in air flow of the used catalysts are reported in Fig. 7, and show two distinct weight losses dependent on the Mg/Al molar ratios. The total weight loss after heating the sample from room temperature to 1173 K for Pd-HT-21 and Pd-HT-31 (after 20 h on stream) and for Pd-HT-41 and Pd-HTR-41 (after 60 h on stream when the final conversion were 80% and 87%, respectively) were around 80% and 87% respectively. In view of the results of MS analysis, these weight losses are attributed to carbonaceous deposits. The inset of the Fig. 7 shows the amount of carbon in the Pd-HT catalysts, determined by TGA as a function of the Mg/Al in the catalyst. These TGA results clearly demonstrate that the Mg/Al molar ratio plays a strong role in the extent of carbon deposition in the catalysts. An increase in the Mg content is beneficial to the suppression of carbonaceous deposits. Particularly the Pd-HTR-41 catalyst showed the lowest weight loss. The rehydration of the Pd-HT-41 sample induced a decrease of the carbon deposits.

The basic properties of the Pd-HT-41 and Pd-HTR-41 were determined by CO_2 -TPD. Fig. 8 shows the TPD trace for two representative samples (Pd-HT-41 and Pd-HTR-41). From the

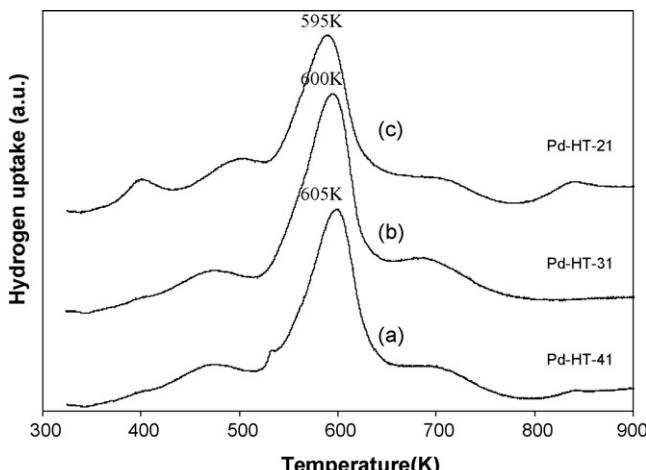


Fig. 4. H_2 temperature-programmed reduction profile of the palladium catalysts. (a) Pd-HT-41, (b) Pd-HT-31 and (c) Pd-HT-21.

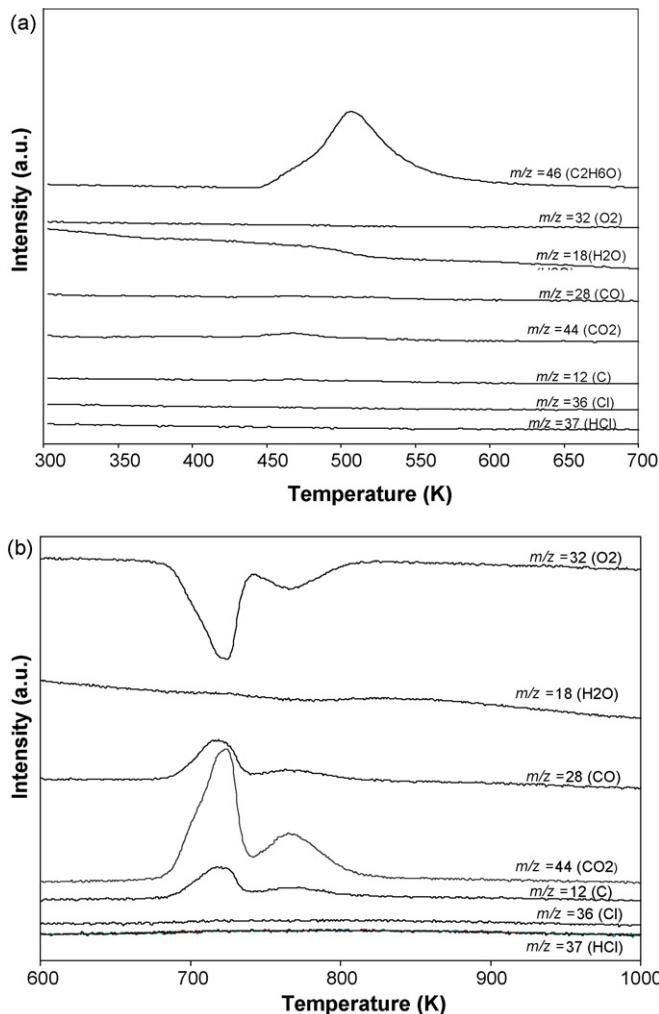


Fig. 5. Mass spectroscopic (MS) of the spent sample Pd-HT-21 showing: (a) traces of the species evolved during the He-TPD and (b) the traces in the sequential analysis of TPO.

quantification of the amount of the CO_2 evolved by integration of the corresponding peaks indicated that Pd-HT-41 and Pd-HTR-41 presented values of 1.43 and 5.03 mmol g^{-1} respectively. A small shift of the peak is also observed from 674 to 705 K which would be indicative of a higher basic strength on the rehydrated sample.

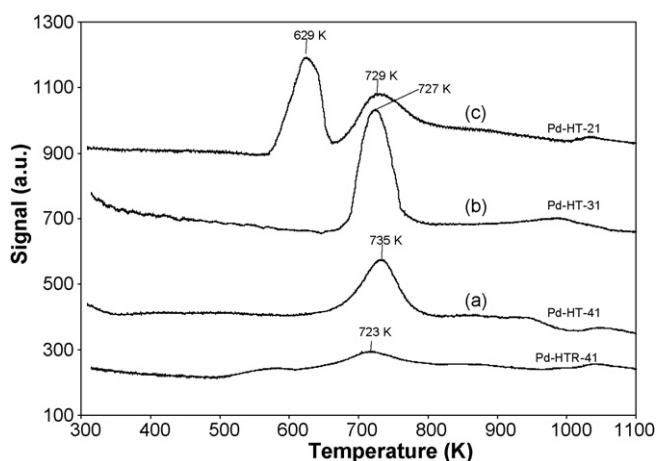


Fig. 6. Temperature-programmed oxidation of the spent Pd hydrotalcite catalysts. (a) Pd-HT-41, (b) Pd-HT-31 and (c) Pd-HT-21.

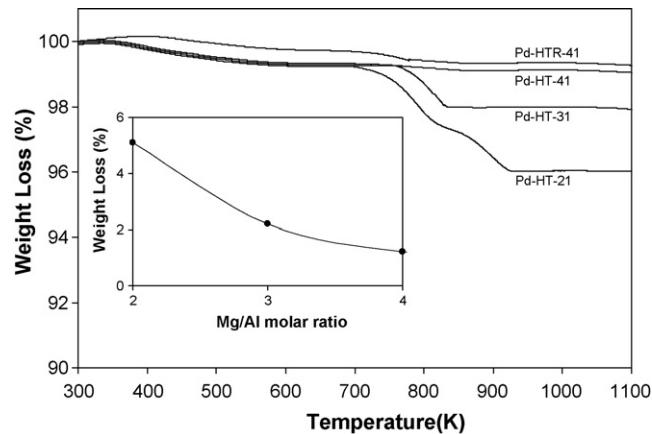


Fig. 7. Thermogravimetric analysis of the spent Pd-HT catalysts. Inset: carbon content in the spent samples versus Mg/Al molar ration.

3.2. Catalytic activity

The gas-phase hydrodechlorination of 1,2,4-trichlorobenzene over Pd-HT catalysts was studied in a temperature range of 323–573 K. The main products detected were benzene, chlorobenzene, *o*-dichlorobenzene and *p*-dichlorobenzene. The products obtained in this study are in line with previous results obtained for hydrodechlorination of 1,2,4-trichlorobenzene on Ni/Niobia [24], Ni/ Al_2O_3 [25], and Ni/Mg/Al hydrotalcite catalysts [26,27]. A blank test run with the different oxide supports showed no conversion of 1,2,4-trichlorobenzene at the same reaction conditions.

The comparison of the different palladium-supported catalysts was performed at a constant mol ratio of $\text{H}_2/1,2,4$ -trichlorobenzene of 182 for all the catalysts at room temperature. Table 2 shows the conversion and product distribution as a function of the temperature, for the conversion of 1,2,4-trichlorobenzene. As temperature increased, the production of benzene increased, whereas chlorobenzene, *o*-dichlorobenzene and *p*-dichlorobenzene decreased. In all cases chlorobenzene and *p*-dichlorobenzene were minor products. Fig. 9 shows the product distribution of Pd-HT catalysts at the same conversion. It clearly shows that an increase of the Mg/Al molar ratio in the support material induced an increase in the selectivity to benzene and a decrease in the selectivity towards the other products. According to these results it is tempting to conclude that the basic character of the catalyst is beneficial for the catalytic performance in the 1,2,4

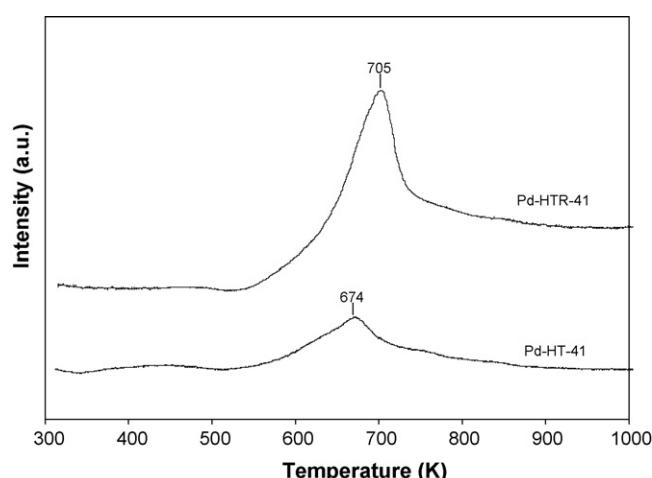


Fig. 8. CO_2 -TPD profiles of the Pd-HT-41 and Pd-HTR-41 samples.

Table 2

Product distribution in function of temperature over the Pd-HT catalysts

Catalyst	T (K)	X (%) ^a	Selectivity (%) ^b			
			Bz	Chl	<i>o</i> -Dichl	<i>p</i> -Dichl
Pd-HT-21	373	25.8	30.3	6.1	50.4	13.2
	433	48.1	46.4	5.1	39.4	9.1
	473	69.4	61.1	4.4	25.2	9.3
Pd-HT-31	373	52.1	61.3	3.6	29.4	5.7
	433	72.6	70.8	2.0	23.2	4.0
	473	84.6	85.0	2.2	11.5	2.3
Pd-HT-41	373	74.6	79.2	5.8	11.9	3.1
	433	88.0	92.0	2.2	4.2	2.7
	473	100.0	100.0	0	0	0

^a X (%): conversion of 1,2,4-trichlorobenzene.^b Bz: benzene, Chl: chlorobenzene, *o*-Dichl: *o*-dichlorobenzene, *p*-Dichl: *p*-dichlorobenzene.

trichlorobenzene hydrodechlorination reaction. Hydrodechlorination is a stepwise process for the elimination of chlorine species, and the lower rates to *o*-dichlorobenzene and *p*-dichlorobenzene formation observed in our experiments may then be related to the inductive and steric effects induced by the Ph-Cl bonds.

The effect of time on stream was studied at 473 K over Pd-HT catalysts. The space velocity of 1,2,4-trichlorobenzene was maintained at 15.6 mg min mmol⁻¹. The study was carried out for 18 h on stream. Conversion decreased with time on stream over all catalysts, as illustrated on Fig. 10. The deactivation of the Pd catalysts for the hydrodechlorination of the 1,2,4-trichlorobenzene appeared to be greatly dependent on the Mg/Al molar ratio of the support. In particular, a comparison between the catalyst Pd-HT-41 and Pd-HT-21 showed that the higher initial activity is associated with a higher Mg content. Pd-HT-21 catalyst showed the highest rate of decay, and Pd-HT-41 was the most stable with time. The selectivity to benzene decreased whereas *o*-dichlorobenzene showed an increase with time. This selectivity to *o*-dichlorobenzene increased probably due to deactivation of the catalyst by blockage of the active sites. Deactivation with time on stream was studied at 473 K over Pd-HT-41 and Pd-HTR-41 catalysts as shown in Fig. 11, using a space velocity of 1,2,4-trichlorobenzene increased by four times (61.6 mg min mmol⁻¹). It appears that the rehydrated catalyst Pd-HTR-41 possesses higher catalytic activity than Pd-HT-41 and a good stability. This is related

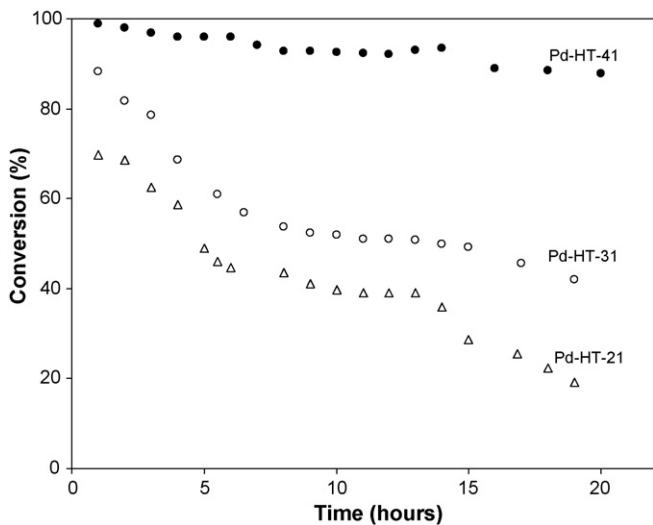


Fig. 10. Conversion versus time of stream of the Pd hydrotalcite catalysts with a space velocity of 15.6 mg min mmol⁻¹. (a) Pd-HT-41, (b) Pd-HT-31 and (c) Pd-HT-21.

to the introduction of Brønsted basic sites that influence the hydrodechlorination activity.

4. Discussion

These catalysts supported by hydrotalcites show good activities, reach nearly full selectivity for benzene, and most surprisingly deactivate very little. The cause of the activity loss was investigated by several means: the presence of carbon in the spent catalysts was confirmed by TPO/MS and TGA shown in Figs. 6 and 7. Both analyses confirmed that carbonaceous species had been adsorbed on the spent catalysts suggesting deactivation by coking. As a result the observed loss in activity can be linked to a blockage of active sites by carbonaceous deposits. By contrast, the contribution of deactivation due to HCl produced in the hydrodechlorination reaction might be negligible when compared with the carbon species. ESEM/energy-dispersive X-ray analysis of the spent samples, as depicted in Fig. 3, revealed residual chlorides and carbon species. However no chlorine was found in the effluents in the mass spectroscopy analysis of the He-TPD and TPO in a given

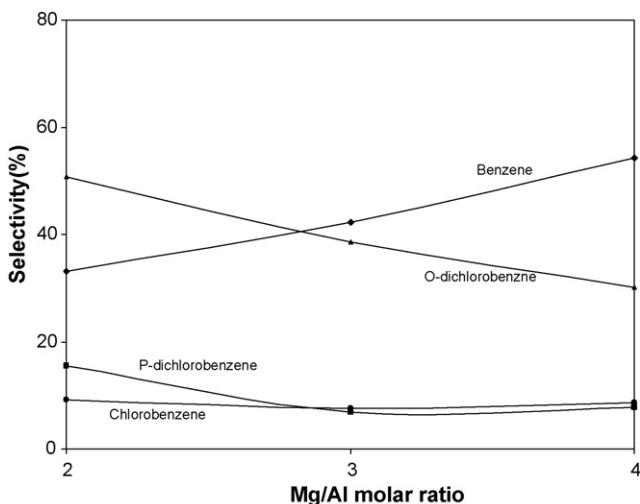


Fig. 9. Selectivity of catalysts at 50% conversion versus Mg/Al molar ratio in the Mg(Al)O support. The reaction temperature was 433 K.

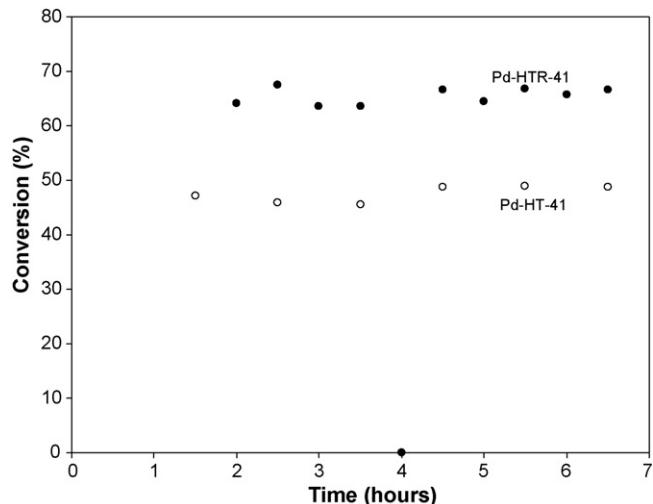


Fig. 11. Comparison in the catalytic performance between Pd-HT-41 and Pd-HTR-41 catalysts versus time of reaction using a space velocity of 61.6 mg min mmol⁻¹.

range of temperature as shown the Fig. 5, therefore the main poison seems to be coke.

The Mg content played a role in the decrease of the carbon content in the samples. The analyses showed that lower amounts of carbon were detected as the Mg/Al molar ratio in our Pd-HT catalysts increased. Different TPO features were observed depending on the Mg/Al molar ratio: the Pd-HTR-41, Pd-HT-41 and Pd-HT-31 sample presented only one peak at about 730 K, while decreasing the Mg content (Pd-HT-21), a second peak appeared at lower temperature with its maximum located around 629 K. It has to be emphasized that two different steps are also observed by thermogravimetric analysis of the combustion of carbonaceous species. An appreciable amount of carbon of about 6% was detected in the spent Pd-HT-21 sample from TGA analysis. The Pd-HT-41 and Pd-HTR-41 samples showed the lowest carbon deposition level with value around 2% and 1% even at larger time on stream (60 h) at the same reaction conditions.

The analysis of spent catalysts by TPO coupled to MS gives an evaluation of HCl, CO₂, O₂ and CO in the outlet gas. The results for CO₂ signal for a representative sample (Pd-HT-21), reported in Fig. 5 confirm that the peaks detected in the TPO measurements correspond to the combustion of carbonaceous deposits. Marécot et al. [28] investigated the deactivation of Pd/SiO₂ deactivated by coke formed by the conversion of cyclopentane. Two peaks were observed in the TPO profiles of coked catalysts, corresponding to coke deposition on the metallic function, since silica has no acidity: the first one near 523 K, was attributed to coke deposited on palladium atoms of high coordination number, and a second TPO peak near 673 K involving palladium atoms of low coordination number. In this hypothesis, the deactivation would be related to the distribution of particles sizes, but since this distribution is only slightly altered by the change of the support, while clear changes of deactivation do occur, it appears difficult to favour this interpretation.

The most stable catalysts show only one peak, which has then to be attributed to carbon deposited on the metallic surface. The comparison of basicities of Fig. 8 suggests that there exists a correlation between basicity and coke deposition on the metallic surface. Indeed as discussed above, an effect of the basicity of the support on the adsorptive and catalytic properties of Pd have been evidenced [15,19]. A basic support acts as a basic additive, introduced from the liquid phase [14]. A faster rate of dechlorination of 1,2,4-trichlorobenzene increases the concentration in dichloro intermediates which can react faster, which accounts for the higher selectivity to benzene. The observation that benzene is not hydrogenated on the most basic catalyst, is also consistent with the report that the activity for benzene hydrogenation on Pd increased on acid supports [29,30]. The mechanism of coke formation is still not clear but could involve reactions of alkylation of aromatics in which Pd is known to be active [31,32]. These reactions are considered to involve oxidized species of Pd [32] which should be unfavoured on basic supports.

5. Conclusion

A series of palladium catalysts supported on several Mg/Al hydrotalcite materials were prepared and studied in the hydro-

dechlorination of 1,2,4-trichlorobenzene. The results were correlated with the basic character of the Mg(Al)O mixed oxide support. It has been shown that palladium catalyst supported on calcined hydrotalcites with higher Mg/Al ratio showed a total conversion of 1,2,4-trichlorobenzene towards benzene at 473 K. Instrumental characterizations of the spent catalysts operated at 473 K revealed that the deactivation arised mainly due to coke deposition on the surfaces and not from the HCl product. The stabilities of the catalysts were also strongly dependent on the Mg/Al of the support. Additionally activation of the Pd-Mg(Al)O sample with Mg/Al molar ratio of four by rehydration enhanced both the catalytic activity and stability. Finally these results indicated the feasibility of hydrotalcite-like and derived materials as catalyst support in the hydrodechlorination reaction of 1,2,4-trichlorobenzene.

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